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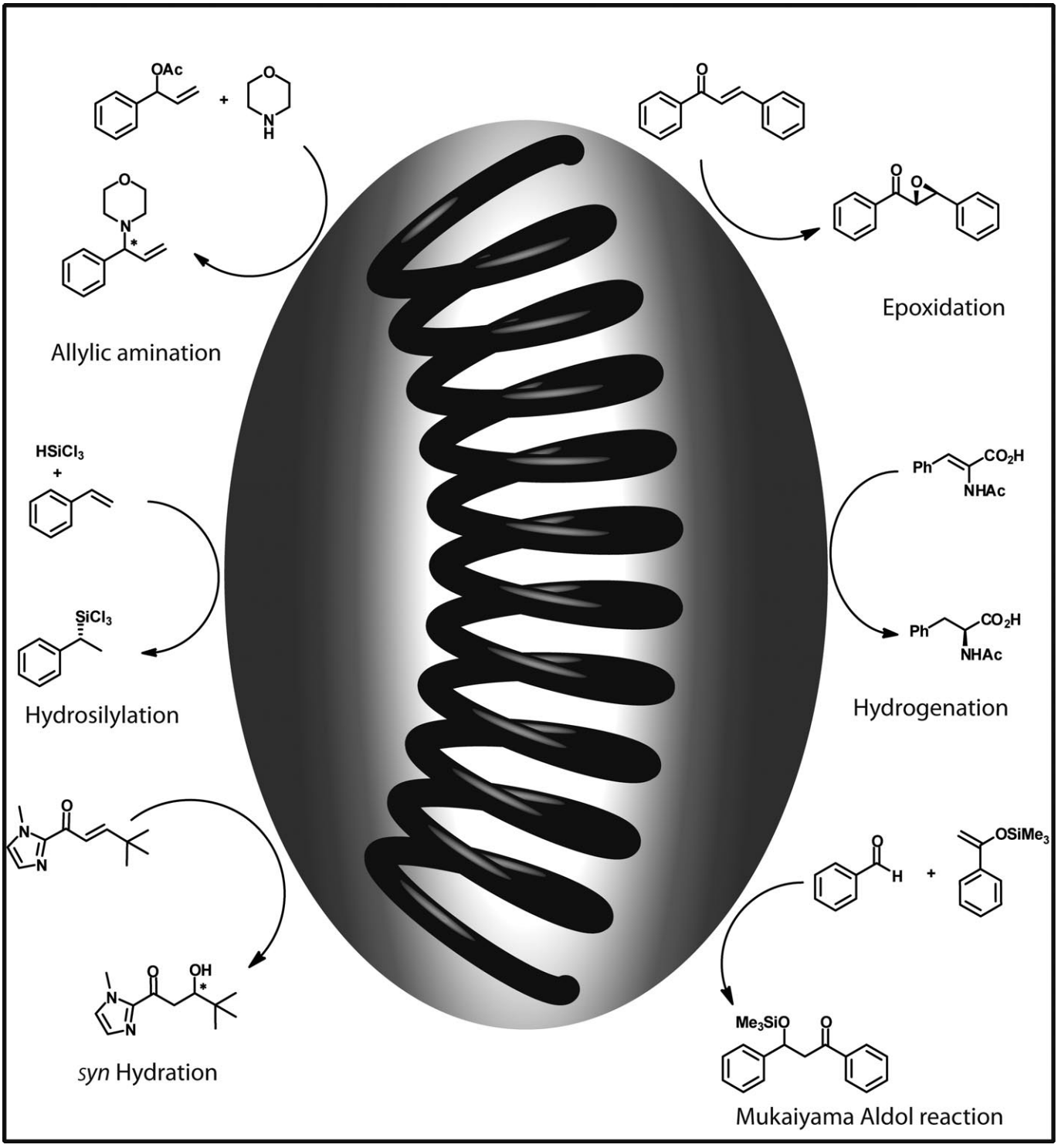
Asymmetric Catalysis with Helical Polymers

Rik P. Megens and Gerard Roelfes*[a]



Abstract: Inspired by nature, the use of helical biopolymer catalysts has emerged over the last years as a new approach to asymmetric catalysis. In this Concept article the various approaches and designs and their application in asymmetric catalysis will be discussed.

Keywords: asymmetric synthesis · biopolymers · DNA · helical structures · organocatalysis · transition metals

Introduction

The helical structure has always had a special attraction to chemists, especially since the discovery of the peptidic α helix[1] and the DNA double helix structures,[2] which have shown that helicity is a key element of biomolecular structure. Many efforts have been dedicated to recreating these helical structures with synthetic macromolecules. This has resulted in a variety of helical polymers that have found widespread applications because of their interesting material properties.[3] Inspired by nature, the use of helical polymers in enantioselective catalysis is starting to be explored. In this Concept article this emerging field will be introduced. We have chosen not to distinguish between biopolymers, such as peptides, polynucleotides, and other polymers. Instead, a more conceptual approach will be presented, focusing on the various design strategies that can be used to achieve asymmetric catalysis with helical polymers.

Helical polymers can be divided into two main classes. First, there are the static helical polymers. These are polymers in which the helical sense is "fixed", that is, it cannot interconvert. This class can be subdivided into 1) polymers in which the helicity originates from the chirality in the side chains and 2) the helical polymers that do not rely on chiral side chains; these include polymers with chiral centers in the main chain, as a result of the use of chiral monomers and stable helical polymers of achiral monomers, which were polymerized in a helix-sense-specific manner. The second main class is that of the dynamic and/or responsive helical polymers. Responsive polymers respond to external physical, chemical, or electrical stimuli resulting in a dramatic change in morphology, structure, shape, or function.[4] These polymers become helical under specific reaction conditions and can interconvert to give the opposite helicity.

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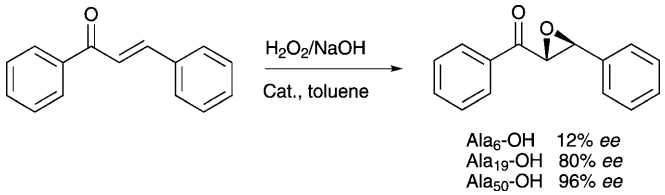
Static helical polymers

Helical polymers with side chain chirality: A variety of polymers need to be equipped with chiral side chains to maintain a stable helical structure in an enantiomerically pure form. In the case of peptides, the choice of the side chains is crucial to obtain a helical structure. Other polymers, for example, polyacetylenes and polyisocynates, do form helical structures by themselves, but their inversion barriers are low. Therefore, to stabilize the helical structure, chiral side chains are required.[3]

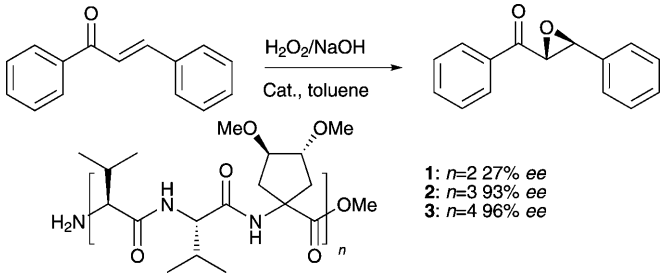
One of the early demonstrations of chiral polymers in catalysis was the use of polypeptides as catalysts in the enantioselective nucleophilic epoxidation of chalcone with hydrogen peroxide, in what has become known as the Julia–Colonna epoxidation.[5–8] Using polyalanine as the catalyst, the epoxide product could be obtained in up to 96% enantiomeric excess (*ee*), depending on the length of the polypeptide (Scheme 1). This was the first indication of a macromolecular amplification of chirality, although a helical structure has not been proven for these peptides.



Scheme 1. Epoxidation of chalcone catalyzed by polypeptides.

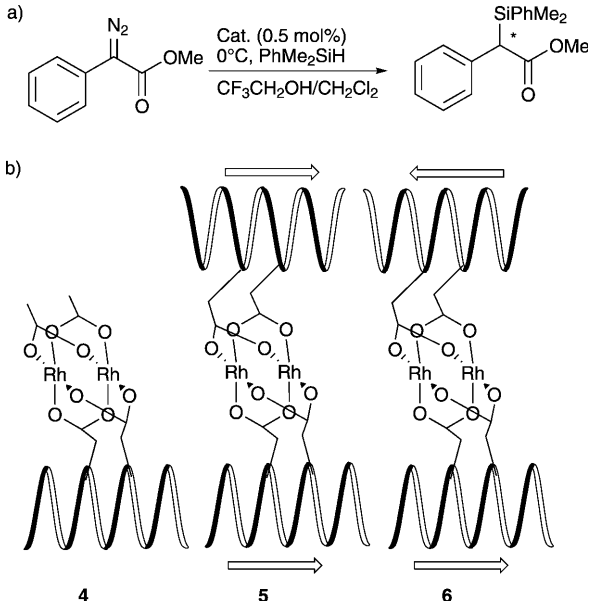
Poly-alanine, leucine, and isoleucine are among the most efficient catalysts for the Julia–Colonna epoxidation, with longer polymer chain giving higher reaction rates and enantiomeric excesses.[6]

More recently, a chiral cyclic α-amino acid oligopeptide for the asymmetric epoxidation of azachalcone was reported. X-ray crystallographic analysis has shown that these oligopeptides (**1**–**3**, Scheme 2) form α-helical structures.[9] An increase in enantioselectivity was observed with increasing peptide length (Scheme 2), which is a similar trend compared to the above-mentioned peptides.



Scheme 2. Epoxidation of chalcone catalyzed by polypeptides **1**–**3**.

Whereas the Julia–Colonna-type epoxidations represent an organocatalytic approach, catalytically active transition-metal complexes can also be incorporated into a helical peptide structure. Ball and co-workers designed a peptide containing two carboxylate side chains that can coordinate to a dirhodium metal center.[10] These metallopeptides proved to be active in diazo decomposition reactions,[11] however, not in an asymmetric catalytic fashion. The design was changed slightly to nonapeptide **4**, which catalyzed the insertion reaction of carbenes into $PhMe_2SiH$ (Scheme 3a) to afford the

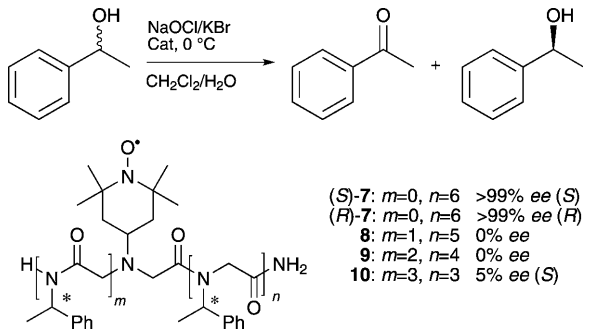


Scheme 3. a) Insertion reaction of $PhMe_2SiH$ into α-diazophenylacetate. b) Different rhodium peptides as catalysts in an insertion reaction.

product in 32% *ee*.[12] To improve the chiral recognition, a bis-peptide catalyst was designed, in which the Asp side chains of two peptides were used to bridge the dirhodium center. (Scheme 3b).[12] The bis-peptide can be parallel (as in **5**) or antiparallel (as in **6**) isomers, however, to date, it has not been established which isomer is which. The bis-peptide isomers afforded different enantioselectivities (20 and 45% *ee*, respectively), which could be further improved by changing the peptide sequence (up to 92% *ee*). It was found that the residues adjacent to the catalytic moiety had the most significant effect on the enantioselectivity.

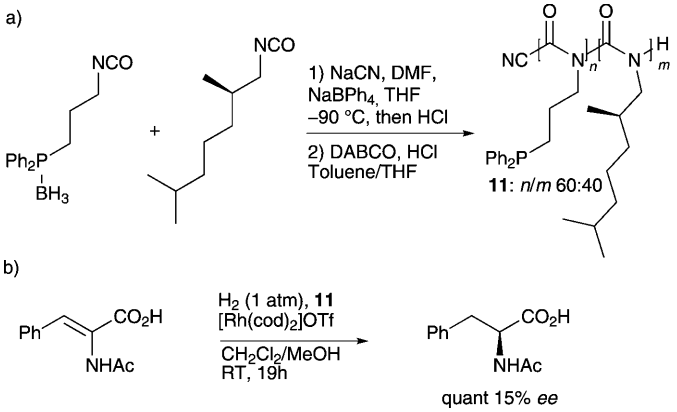
Small peptoids have been used in the oxidative kinetic resolution of 1-phenylethanol by attaching 2,2,6,6-tetramethylpiperidine *N*-oxide(TEMPO), a well-known oxidation catalyst[13] (Scheme 4).[14] It was found that right-handed helical **7** preferentially oxidized (*S*)-1-phenylethanol to acetophenone, whereas left-handed **7** preferentially oxidized (*R*)-1-phenylethanol. Furthermore, the enantioselectivity was dependent on the position of the catalytic moiety within the peptide: a decreased enantioselectivity was found with the TEMPO in internal positions (compounds **8**–**10**, Scheme 4).

The first example using a nonpeptidic polymer involved a polyisocyanate in which an achiral monomer containing a



Scheme 4. Oxidative kinetic resolution of 1-phenylethanol.

phosphine ligand was co-polymerized with a chiral non-metal-binding monomer (Scheme 5a).[15] In this way, a single-sense helical polymer was created using a sub-stoichiometric number of chiral units.

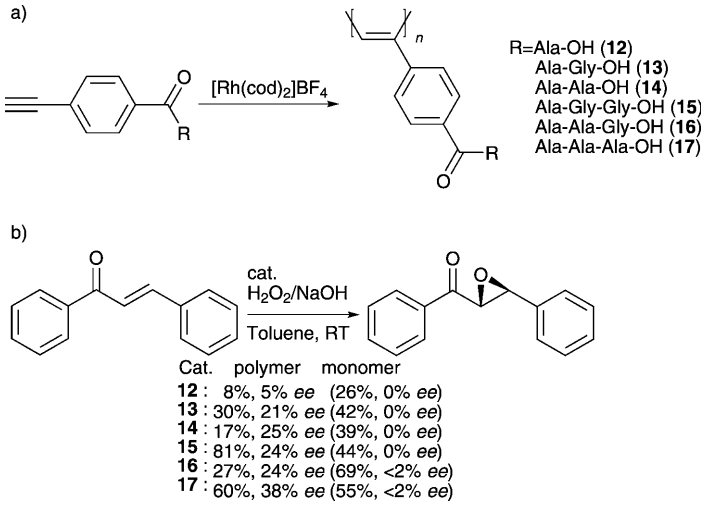


Scheme 5. a) Synthesis of polyisocyanate copolymers. DABCO = 1,4-diazabicyclo[2.2.2]octane. b) Rhodium-catalyzed asymmetric hydrogenation of N-acetamidocinnamic acid.

Upon complexation with $[Rh(cod)_2]OTf$, (cod = 1,5-cyclooctadiene) the co-polymer catalyst **11** was applied in the asymmetric hydrogenation of *N*-acetamidocinnamic acid. However, only low enantioselectivity of the hydrogenated product was achieved (Scheme 5b).

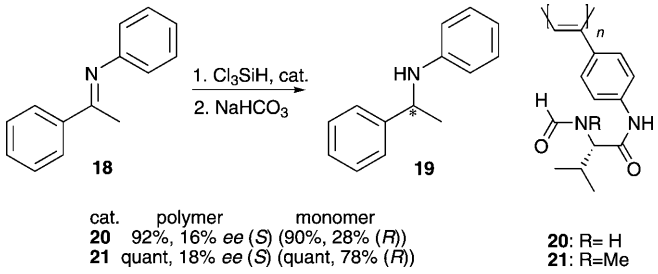
The use of peptides as side chains can have a dual role; they are used to stabilize the helical structure of the polymer but can also be used as an organocatalyst.[16] For example, a poly(phenylacetylene) with pendant oligopeptide arms was shown to adopt a stable helical structure. Application of these polymers in the epoxidation of chalcones using H_2O_2 gave rise to moderate enantioselectivities of up to 38% (Scheme 6b). Since with the corresponding monomers no significant *ee* value was obtained, it was suggested that the selectivity originates directly from the helical polymer and not from the chiral peptides.[17]

However, when the chiral side chains themselves do give rise to enantioselectivity, there is the potential of a mismatch with the sense of helicity. This was observed in the reduction of ketimine **18** catalyzed by **20** or **21**.[18] The reaction



Scheme 6. Helical poly(phenylacetylene)s with oligopeptide pendants; a) polymer synthesis. b) epoxidation of chalcone catalyzed by helical polymers **12**--**17**.

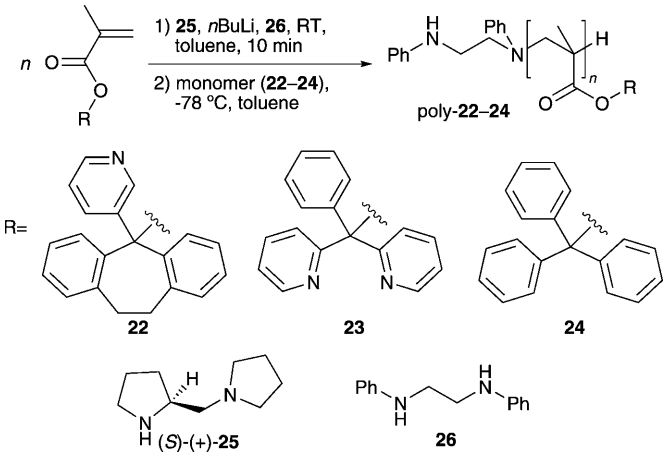
catalyzed by the polymer gave a low *ee* value of the opposite enantiomer compared to the monomer (Scheme 7). This indicates that the chirality of the side chain and the helicity of the main chain of the polymer counteract each other (mismatched combination), resulting in low overall enantioselectivities.



Scheme 7. Asymmetric reduction of ketimine catalyzed by **20** or **21**.

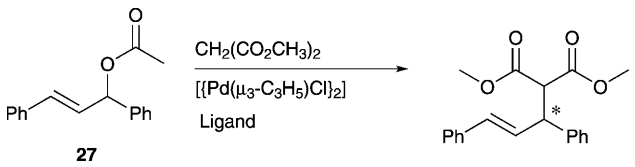
Helical polymers that do not contain chiral side chains: Enantioselective polymerization can give access to helical polymers that do not require chiral side chains, provided that their helical structure is stable.[19,20] In this process, the chirality in the polymer is induced during the polymerization by using a chiral initiator.

The group of Reggelin prepared helical polymers (poly-**22**–**24**) by helix-sense selective anionic polymerization of methacrylates containing a pyridyl metal-binding moiety using a chiral initiator. This initiator was made by treating a mixture of (*S*)- or (*R*)-1-(2-pyrrolidinomethyl)pyrrolidine (**25**) and *N*,*N*′-diphenylethylenediamine (**26**) with one equivalent of *n*BuLi (Scheme 8). This forms a chiral base complex, which is able to initiate the helix-sense-selective anionic polymerization.[15,21]



Scheme 8. Anionic helix-sense selective polymerization of methacrylates.

These polymers were used in the palladium-catalyzed enantioselective allylic substitution reaction of 1,3-diphenylprop-2-enyl acetate (**27**) with dimethylmalonate (Scheme 9).

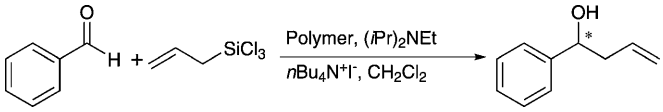


Scheme 9. Allylic alkylation of 1,3-diphenylprop-2-enyl acetate with dimethylmalonate.

It was found that using **26** in the catalysis did not give rise to any conversion.[21] Initiator **25** did result in conversion, with a slight enantiomeric excess of 10%. However, when (−)-poly-**22** was used, the product was obtained in 81% yield and with 33% *ee*. Using the polymer with the opposite helicity resulted in preferred formation of the opposite enantiomer of the product with a similar enantioselectivity (32% *ee*).

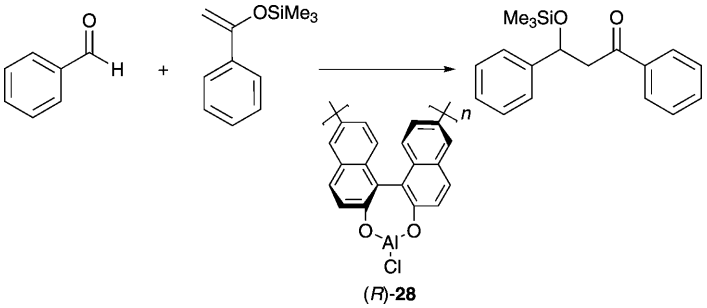
Poly-**23**, which contains bidentate ligands, was designed because precipitation of palladium was observed when using the monodentate ligands.[15] A low optical activity was observed, which most likely indicates that a low excess of one of the helical forms of the polymer is present. Therefore, also a copolymer of **23** and **24** (poly(**23**-co-**24**)) was prepared, which gave rise to an increased enantioselectivity of 60%.

It was demonstrated that by oxidizing the pyridyl group to the corresponding pyridyl *N*-oxide with *meta*-chloroperbenzoic acid (*m*CPBA), these polymers could be used as Lewis base catalysts.[22] The *N*-oxide, derived from polymer **22**, proved to be active in the asymmetric allylation of benzaldehyde with allyltrichlorosilane (Scheme 10), resulting in the formation of the secondary alcohol in 56% yield and with 19% *ee*. In contrast, no reaction was observed with polymer **22**.



Scheme 10. Asymmetric allylation of benzaldehyde with allyltrichlorosilane.

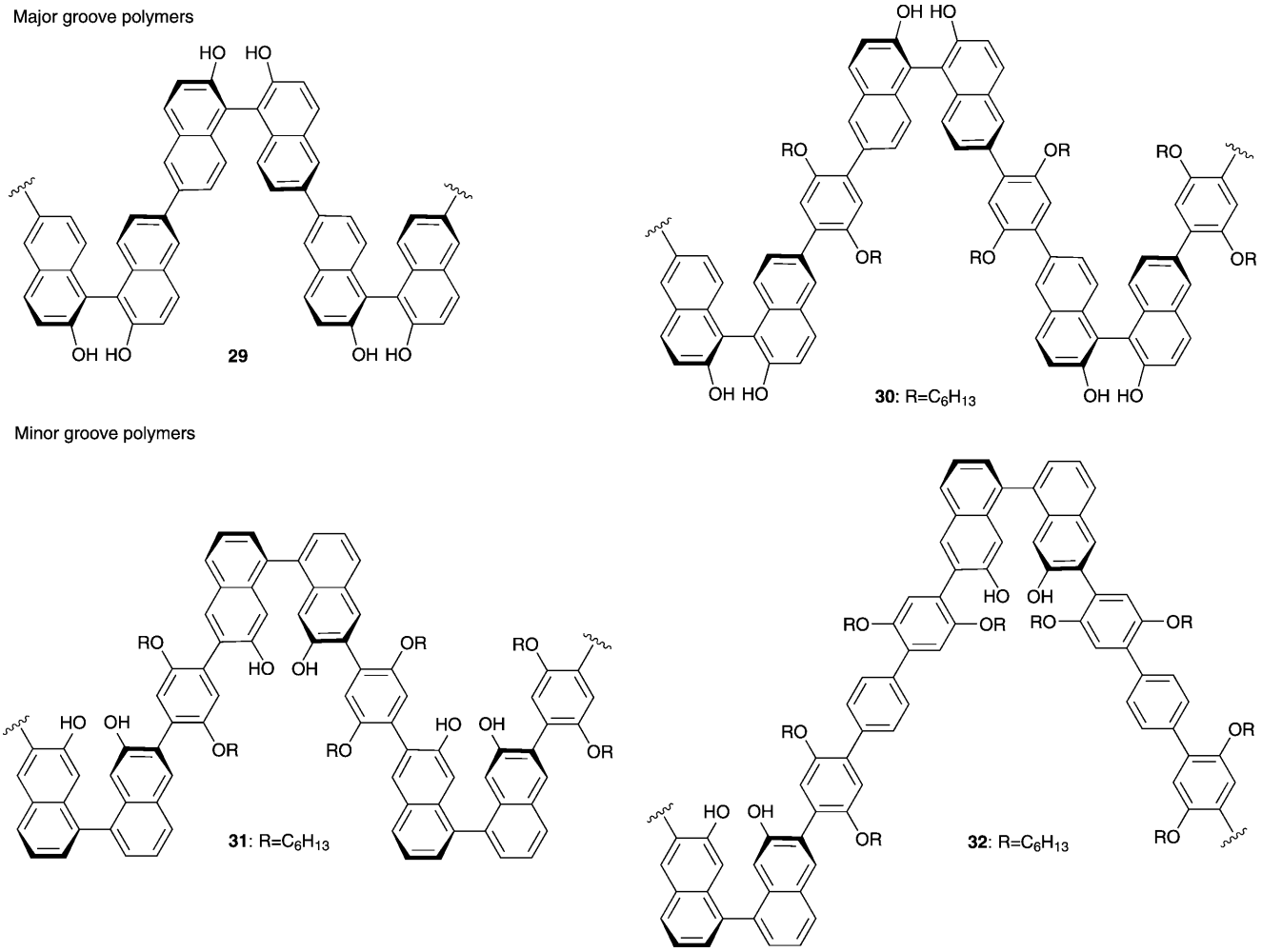
Using chiral monomers can also give rise to the formation of conformationally stable helical polymers. Binaphthols have been applied extensively in asymmetric organic reactions and have been shown to induce excellent chiral selectivity in many reactions.[23,24] Pu and co-workers, have used polybinaphthols to form rigid and sterically regular polymers. The polybinaphthol was treated with aluminum chloride and then used as a Lewis acid catalyst in the Mukaiyama aldol reaction (Scheme 11).[25,26] Using the polymer **28** full conversion was obtained after 3.5 h, whereas the monomeric aluminum complex gave only about 5% conversion in the same time. However no enantioselectivity was observed in either case.



Scheme 11. Mukaiyama aldol reaction.

Polybinaphthyls (such as **29**–**32**) have been proposed to posses a "major" and a "minor" groove.[27,28] The 6,6′-polymerized binaphthols, in which the hydroxy groups point outwards, are designated as "major-groove" polybinaphthyls. When the binaphthol is polymerized at the 3,3′-position, a "minor-groove" polymer is obtained, with the hydroxy groups pointing inwards in the helical structure. A variety of minor and major groove polymers have been prepared (Scheme 12).[27–29]

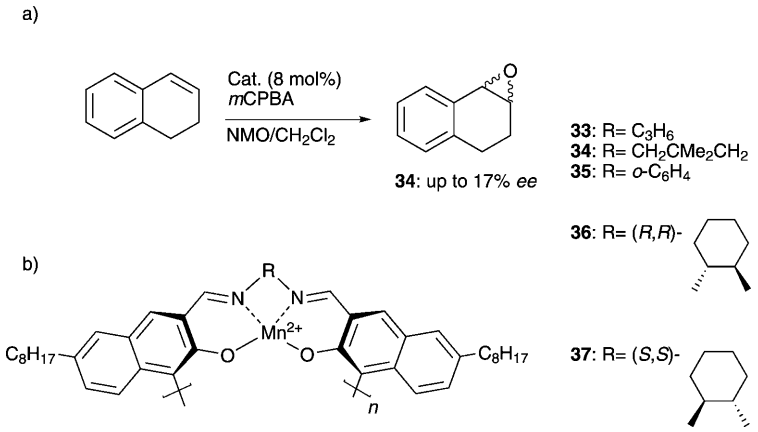
When the 1,2-addition reaction of benzaldehyde with diethylzinc was performed using the major groove polymers



Scheme 12. Variety of polybinaphthyls used as ligand in the reaction of benzaldehyde with diethylzinc.

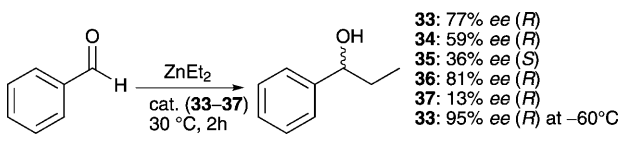
29 and **30**, a rather low enantioselectivity was obtained and also considerable amounts of benzylalcohol were found as a side product.[27] Using the minor groove polybinaphthyl **31**, high chemo- and enantioselectivities were obtained; by extending the spacer between the binaphthyl units of **32** the selectivity could be further increased up to 98% *ee*.[29] This demonstrates the importance of the position of the catalyst in the polymer. These polymers were recovered readily by precipitation with methanol and used again without loss of activity and selectivity.[30]

A similar approach was followed by Takata and co-workers by using a poly(binaphthyl salen metal complex).[31,32] Salen manganese complexes **33**–**35** were shown to be capable of oxidizing alkenes, albeit with low enantioselectivity (Scheme 13a).



Scheme 13. a) Epoxidation of alkenes with **34**. b) Poly(binaphthyl salen mangenese complex).

When the same polymers were used in the 1,2-addition of diethylzinc to benzaldehyde excellent yields and enantioselectivities (e.g., up to 81% *ee* for **36**), were obtained (Scheme 14), which could further be increased to 95% *ee* by lowering the temperature to −60°C. Furthermore, a matched and mismatched combination was observed when introducing chirality into the amine linker.[32]



Scheme 14. Addition of diethylzinc to benzaldehyde.

Undoubtedly, the archetypical helical polymer is DNA. Its unique double helical structure has been a source of inspiration for catalyst design. Asymmetric catalysis with DNA can be divided into two classes that differ in the mode of attachment of the catalytic moiety, that is, using a covalent linkage or through noncovalent interactions.[33–35]

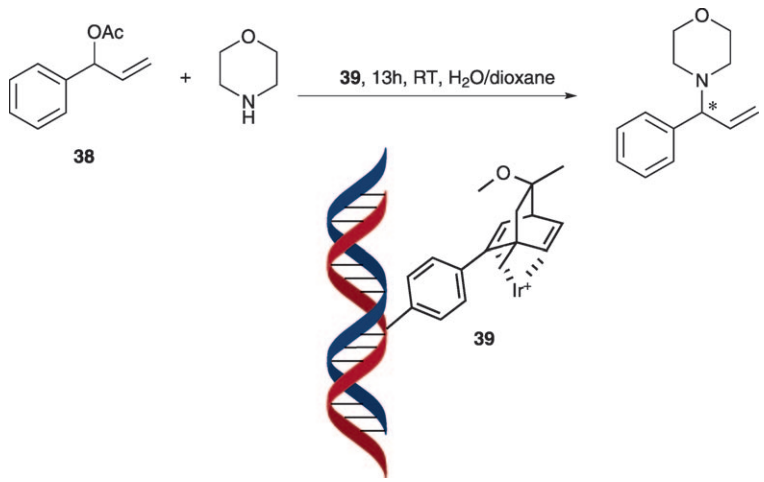
Covalent approach: Covalent anchoring involves binding of a transition-metal complex through the ligand to the DNA using a small spacer moiety. Attachment sites in this case can be modified nucleobases or phosphate esters. Covalent anchoring is attractive, since it allows for precise control over the positioning of the catalyst and, therefore, the structure and microenvironment of the catalytic site. However, covalent modification of DNA is laborious and very time consuming, which complicates the catalyst optimization process. This is illustrated by the fact that several approaches to the synthesis of ligand–DNA conjugates have been reported,[36–38] but in only a few cases successful catalysis have been achieved.

Jäschke and co-workers covalently attached diene ligands to DNA by reaction of the diene ligand with an activated nucleoside 4-triazolyldeoxyuridine, which was introduced by solid-phase synthesis.[39] The corresponding Ir complex **39** proved to be an efficient catalyst for the allylic amination of **38** with morpholine, resulting in the kinetic resolution of **38** (Scheme 15). The enantioselectivity of this reaction was modest (23%) and can be attributed to the chirality of the ligand itself, which gives 28% *ee* in the allylic amination reaction. However, when a complementary RNA strand was used, the opposite enantiomer of the product was formed in 27% *ee*, which indicates that a relationship exists between the structure of the polynucleotide and the enantioselectivity of the catalyzed reaction.

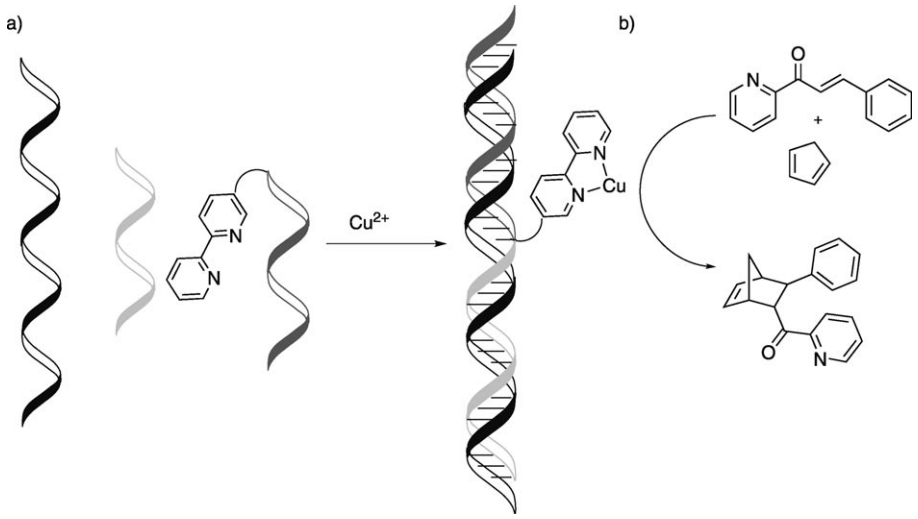
A method that allows for easier optimization involves the modular assembly of a DNA-based catalyst. This strategy involves two oligonucleotides, ON1 and ON2, with a covalently attached 2,2′-bipyridine ligand at the terminus of one of the strands (Scheme 16).[40] Upon hybridization of both oligonucleotides with a complementary template strand, the catalytic moiety is placed in an internal position in the DNA duplex. Complexation of Cu^{2+} to the bipyridine moiety produced the DNA-based catalyst, which was found to be active in the asymmetric Diels–Alder reaction of azachalcone with cyclopentadiene. Enantiomeric excesses of up to 93%, were obtained, depending on the DNA sequence around the catalytic site and the length of the spacer.

Noncovalent approach: Alternatively, a transition-metal complex can be bound to the DNA using supramolecular interactions such as intercalation and/or groove binding. (Figure 1).

The supramolecular anchoring approach is attractive because the catalyst is spontaneously self-assembled by combining the transition-metal complex with the DNA; usually with salmon testes DNA (st-DNA), which allows for rapid optimization. However, depending on the binding affinity



Scheme 15. DNA-based Ir-catalyzed allylic amination.



Scheme 16. a) Modular assembly of a DNA-based system as catalyst for the Diels–Alder reaction. b) The Diels–Alder reaction of azachalcone with cyclopentadiene.

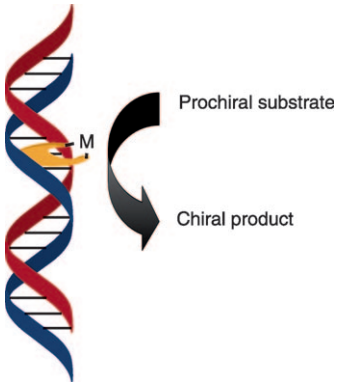
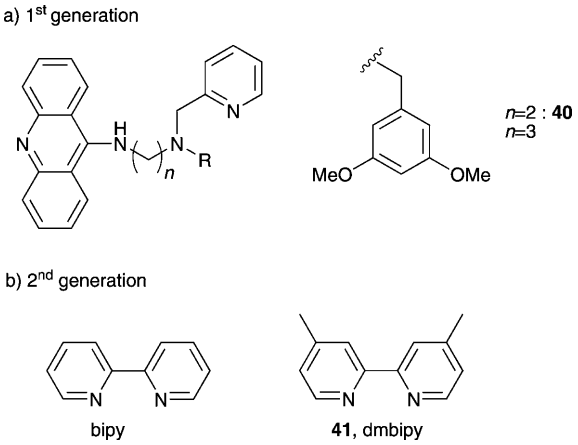


Figure 1. Schematic representation of noncovalent DNA-based catalysis. M = transition-metal ion.

and the DNA sequence selectivity, the catalyst may not be very well defined; it is likely that the transition-metal complex binds at multiple positions to the DNA. This method results in a heterogeneous mixture of catalysts that reside in a different micro-environment and therefore will have different reactivity and selectivity.

The noncovalent approach to DNA-based catalysis has proven highly successful in a variety of reactions.[39,40] The Diels–Alder reaction of azachalcone with cyclopentadiene was used initially to demonstrate the concept and has been used as the benchmark reaction for mechanistic studies. Using the first generation of ligands, which contain separated DNA intercalation and metal binding moieties that are connected by a spacer, up to 50% *ee* was found for this reaction (Scheme 17a).[41]

By changing the design of the ligand, in particular, the length of the spacer, the opposite enantiomer of the product could be obtained, which is of interest since natural DNA is available in one chiral form only. With the second generation of ligands (Scheme 17b), which do not contain a separate DNA binding moiety, up to 99% *ee* was obtained in the case of 4,4′-dimethyl-bipyridine (**41**).[42] The corresponding Cu^{2+} complex, however, has only a moderate DNA-binding affinity and displays no sequence selectivity in binding. Moreover, the DNA binding

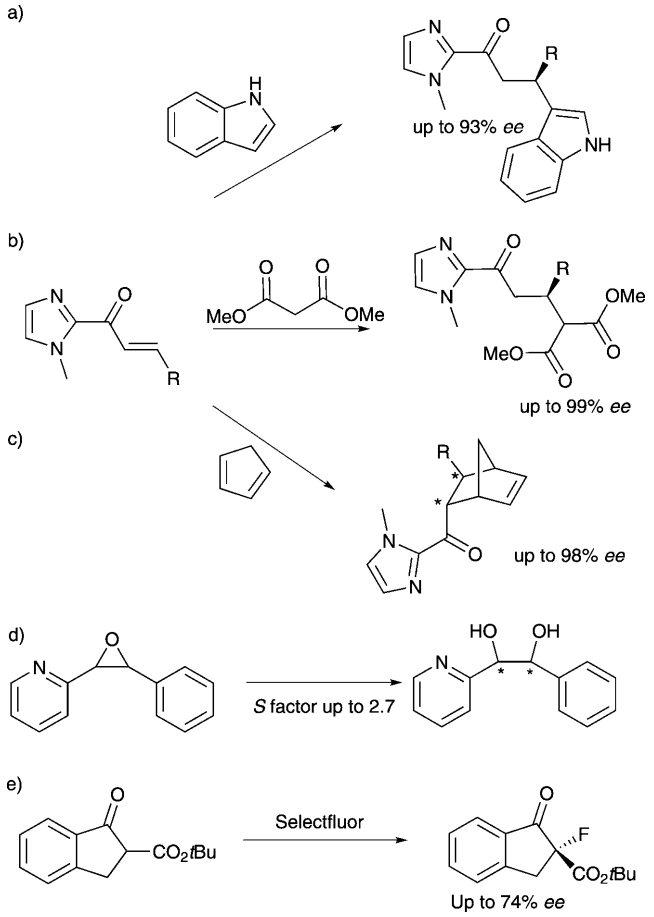


Scheme 17. Different DNA-binding ligands.

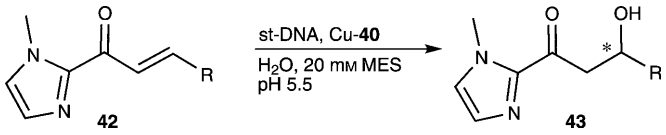
mode is not well defined. In this light, the observed complete enantioselectivity is quite remarkable. This seeming paradox was solved by a kinetic and sequence dependence study, which revealed that the reaction is accelerated up to two orders of magnitude when the catalyst is bound to DNA. Thus, the DNA is not just the chiral scaffold, but also participates actively in the reaction, most likely by providing favorable "second-coordination-sphere interactions".[34,43] Moreover, both the rate acceleration and the enantioselectivity were found to be sequence dependent; the DNA sequences that gave the highest *ee* values also provided the largest rate acceleration.[44,45] These factors combined, it means that although the catalyst is a heterogeneous mixture of many different species, this does not present a problem; those that are in the optimum microenvironment give the highest *ee* values and dominate the outcome of the catalyzed reaction, since they also accelerate the reaction the most.

In addition to the Diels–Alder reaction, the Cu-dmbipy/st-DNA catalyst has been applied successfully in catalytic enantioselective Michael addition,[46,47] Friedel–Crafts alkylation,[48] fluorination,[49] and epoxide ring-opening reactions,[50] with, in several cases, *ee* values of >90% (Scheme 18). As with the Diels–Alder reaction, it was found that the role of DNA in most of these reactions is not limited to that of the chiral scaffold but that also the reaction rate is affected.

Recently it has also been demonstrated that DNA-based catalysis can be applied to a reaction for which there is no precedent using a synthetic catalyst, namely the catalytic enantioselective and diastereospecific *syn* hydration of enones (Scheme 19).[51] In contrast to the other examples of DNA-based catalysis, the first generation ligands, that is, those based on a 9-aminoacridine intercalating moiety, proved to be the most effective ligands for this reaction, giving up to 79% *ee*, which could be further improved to 82% *ee* by performing the reaction in D_2O.



Scheme 18. Reaction scope of DNA-based catalysis. a) Friedel–Crafts alkylation. b) Michael addition. c) Diels–Alder reaction. d) Kinetic resolution of pyridyloxiranes. e) Fluorination reaction.



Scheme 19. Catalytic enantioselective *syn* hydration of enones.

Dynamic and chirality-responsive helical polymers

Responsive polymers are polymers that react to external physical, chemical, or electrical stimuli, resulting in a dramatic change in morphology, structure, shape, or function, such as, for example, helix inversion.[4] To date, a significant number of stimuli-responsive polymers have been synthesized. Most often the chirality-responsive helical polymers contain functional pendant groups and, upon addition of a chiral molecule, a conformational change of the polymer can be induced through noncovalent interactions (Figure 2).[52] These helical structures can be interconverted from right handed to left handed and vice versa as in the case of polyisocyanates and poly(phenylacetylene).[53,54]

To date, only a few examples of asymmetric catalysis with responsive helical polymers have been reported. Yet, catalysts based on responsive helical polymers have great potential, because switching the helicity of the polymer with an external trigger makes it, in principle, possible to selectively

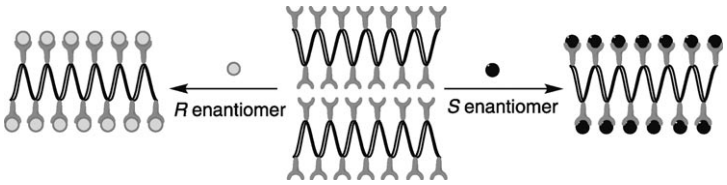
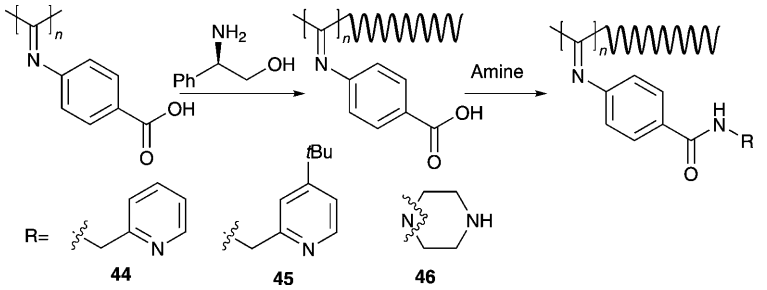


Figure 2. Schematic representation of a chirality-responsive polymer.

obtain either enantiomer of a reaction product using the same catalyst.

In the first example, a poly(4-carboxyphenyl isocyanide) was prepared and, upon addition of (*R*)-phenylglycinol, a single-handed helical structure was induced with a molar ellipticity at 357 nm of $-10.6\,\mathrm{M^{-1}\,cm^{-1}}$.[55] The induced helicity was memorized, since after removal of the chiral amine and



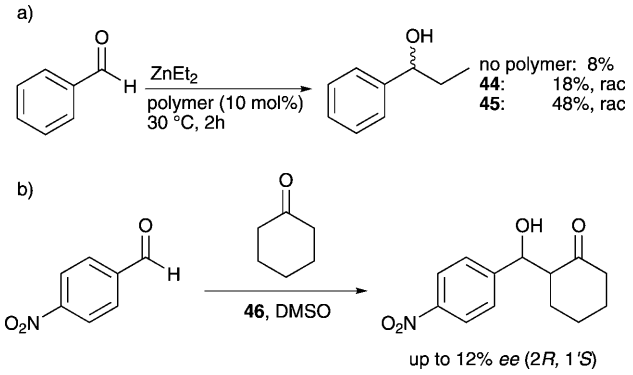
Scheme 20. Schematic illustration for the helicity induction and memory of poly(4-carboxyphenyl isocyanide).

derivitization with an achiral amine containing a ligand moiety, the helical structure remained stable (Scheme 20). The amide moieties were found to increase the thermal stability of the helical polyisocyanide.[56]

Using the polymers derivatized with pyridyl amines in the 1,2-addition reaction of diethylzinc to benzaldehyde (Scheme 21 a) an acceleration of the reaction rate was observed. However, no enantioselectivity was observed, which was attributed to the distance of the pyridyl group from the helical polymer.

The piperazine-bound helical polyisocyanide **46** was used as an organocatalyst in the aldol reaction of benzaldehyde with cyclohexanone. Enantioselectivity was observed, however, the *ee* values were rather low, that is, up to 12% (Scheme 21 b).

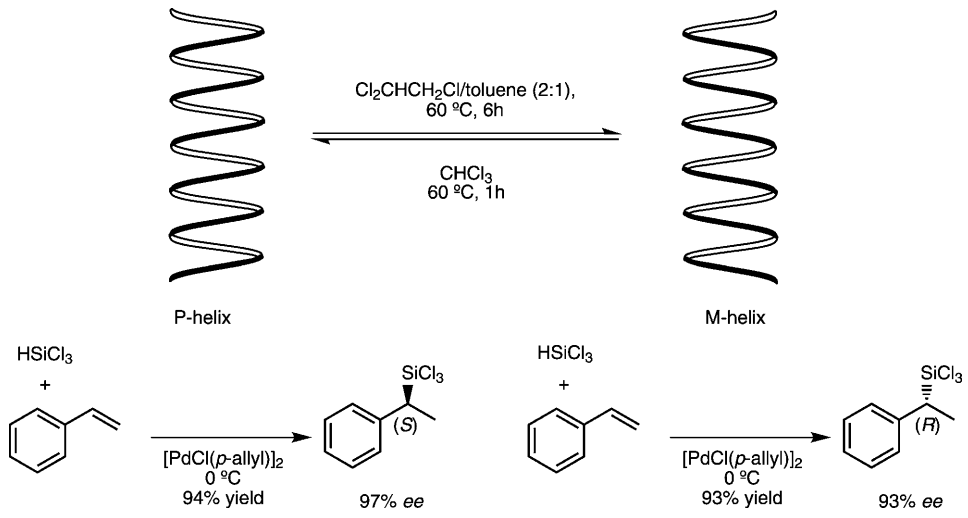
An impressive demonstration of how helix interconversion can be used in asymmetric catalysis was recently reported by Suginome and co-workers.[57] They prepared a high-molecular-weight polymer based on a 20-mer polyquinoxaline-based phosphine (PQXphos) and used it in the palladium-catalyzed asymmetric hydrosilylation of styrenes (Scheme 22). Surprisingly, it was found that this polymer switches from P- to M-helicity upon changing the solvent from chloroform to 1,1,2-trichloroethane/toluene (2:1). This resulted in 97% *ee* of the *S* enantiomer with the P-helical form and 93% *ee* of the *R* enantiomer with the M-helical form. Furthermore, the polymer was recycled up to eight times without loss of selectivity; however, the palladium did have to be recharged at the end of the 8th run as a result of leaching.



Scheme 21. Reaction catalyzed by polymers with helical memory. a) addition of diethylzinc to benzaldehyde. b) Aldol reaction of benzaldehyde with cyclohexanone.

Summary and Outlook

In catalysis, polymers were for a long time only considered as scaffolds to create "heterogeneous" versions of homogeneous catalysts, with the idea that this would facilitate the recovery and recycling of the catalyst .[58] From the examples described here, it is clear that asymmetric catalysis using helical biopolymers has started to emerge as an attractive new approach. This is mainly due to the fact that these helical polymers can provide a chiral microenvironment for a catalyst that is analogous to an enzyme active site, which can be used to direct the catalyzed reaction towards the selective formation of one enantiomer of a product. To date, the biopolymer-based catalysts, for example, peptide- and polynucleotide-based catalysts, have proven to be the most versatile and can already be used in a variety of important catalytic enantioselective reactions. The synthetic polymers have, to date, generally not achieved the same level of activity and selectivity in catalysis. One



Scheme 22. Asymmetric hydrosilylation using a chirality-responsive polymer.

main difference, of course, is that synthetic polymers presently have less functional diversity; they are built up from a smaller number of different monomeric units and are not monodisperse and structurally less well defined compared with biopolymers. However, further advances in polymer preparation to address these issues can be envisioned. Using dynamic and responsive polymers, new avenues in catalysis can be explored, such as using one catalyst to selectively prepare either enantiomer of a product, just by triggering a helix interconversion. Taken together, it can be concluded that helical biopolymers are a promising and attractive new approach to enantioselective catalysis.

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